EFFECT OF PRESSURE ON CATALYST ACTIVITY AND CARBON DEPOSITION DURING CO$_2$ REFORMING OF METHANE OVER NOBLE-METAL CATALYSTS

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Abstract: The reforming of methane with CO$_2$ was studied over 1wt% Rh/alumina, Pt/ZrO$_2$, and Ce-promoted Pt/ZrO$_2$ catalysts at 800$^)$C and pressures of 1, 8, and 14 bar. It was found that high pressure resulted in greater carbon formation, lower methane and CO$_2$ conversions, as well as a lower H$_2$/CO ratio. Temperature-programmed oxidation (TPO), of the catalysts after reaction, shows several CO$_2$ peaks for the Ce-promoted catalyst, indicating several sources or types of carbon and/or several locations on the catalyst are involved with carbon deposition. The change in the temperature and intensity of the TPO peaks with pressure indicates that more stable carbon is deposited at high pressure. Thermodynamic calculations for the endothermic reaction of CH$_4$ with CO$_2$, CH$_4$ decomposition, and CO disproportionation were also performed. The results of these calculations are consistent with CO disproportionation being a larger contributor to carbon deposition at high pressure.

1.   INTRODUCTION

The focus of this work is to test new and novel catalysts with the potential for the cost-effective production of synthesis gas, with the required H$_2$/CO ratio, for use as a Fischer-Tropsch feed stock. Industrially, synthesis gas (syngas) is produced via steam reforming of natural gas using nickel

catalysts at high temperatures and pressures [1]. However, synthesis gas made by steam reforming has an H_2/CO ratio higher than needed for various industrial processes (Fischer-Tropsch, methanol and dimethyl ether synthesis). The cost of syngas production in a process that converts natural gas to liquid fuels is estimated to be 60-70% of the total cost [2]. Much of this cost is due to addition of excess steam or oxygen to the system for reducing carbon formation [2]. Continued carbon deposition leads to catalyst deactivation and eventually plugs the reactor. Therefore, developing new and novel catalysts that operate at a lower H_2O/carbon or O_2/carbon ratios, without forming significant amounts of carbon, is essential for producing cheaper and cleaner transportation fuels.

Recently, many researchers have concentrated their efforts toward catalytic reforming of methane with carbon dioxide [3-6]. This reaction is very useful for chemical utilization of these two major greenhouse gases (CO_2 and methane) into useful feedstock. It also produces a H_2/CO ratio near one that can be used for adjusting H_2/CO ratio in steam reforming, suitable for producing methanol or Fischer-Tropsch products. Although this reaction requires a very large energy input, this is not the only cost consideration. When estimating the cost of fuel production from CO_2 reforming of methane, it is important to consider the source and cost of CO_2 recovery as well as the heat source to drive the reaction. For instance, the cost of CO_2 recovery is much less in a system where the CO_2 is recycled compared to capturing CO_2 from a diluted source [7]. Since the cost of CO_2 recovery factors into the economics of producing fuels via this reforming reaction, it would be desirable to develop catalysts that can operate without carbon build up as close to a stoichiometric ratio as possible.

An economically viable gas-to-liquid process for converting natural gas into synthesis gas requires a catalyst that is active, selective, has a reasonable lifetime, and works at a lower steam/carbon or oxygen/carbon ratio without carbon build up. Finding a solution to carbon build up is made more difficult by the presence of several carbon-forming reactions on the conventional steam reforming, nickel-based, catalysts. Nickel catalyzes carbon formation via hydrocarbon decomposition and CO disproportionation reactions and these reactions greatly contribute to catalyst deactivation, especially at higher pressures [8-10].

High pressure, however, is an essential operating condition for the efficient and cost effective production of synthesis gas. In addition, most downstream processes that use synthesis gas operates at high pressure and downstream compression for these applications would considerably increase the overall process costs. It has been recommended that syngas production and dry reforming be conducted at pressures higher than 10 atm (10.1 bar) [11].

One mechanism for the reaction of CH_4 and CO_2 suggests that these species are activated on the metal particles, with metal-support interactions also playing a role. CH_4 dissociates into CH_x species and carbon, and CO_2 generates CO and adsorbed oxygen (O_{ad}), which is consumed by reacting with CH_x and carbon [12]. If the rate of carbon formation is greater than the rate of carbon oxidation then carbon will accumulate on the surface eventually plugging the reactor.

The use of promoters is one strategy that has been used to circumvent carbon deposition. Stagg and Resasco reported that addition of promoters has multiple effects such as stabilizing surface area, increasing density of CO_2 adsorption sites near the metal particle, and inhibiting the metal particle growth under reaction conditions [13]. A recent literature survey concluded that there are a number of intrinsic properties (metal geometric structure, metal electronic structure, the support, and metal-support interaction) that may influence carbon deposition on methane-dry-reforming catalysts [14]. Manipulating these properties through the use of promoters is one way of reducing carbon deposition.

In this paper we report the effects of pressure on carbon deposition during methane dry reforming reactions on promoted and unpromoted noble metal catalysts.

2.   EXPERIMENTAL

Rhodium, 1wt% on alumina powder, catalyst was purchased (Alfa Aesar). The Pt/ZrO_2 and Ce-promoted catalysts were prepared as described by Stagg and Resasco [13]. The catalysts were reduced at 500^{J}C for one hour before the reaction. The dry reforming reactions were performed in a fixed-bed reactor at 800^{J}C and GHSV = 6 x 10^5 cm^3 g^{-1} h^{-1}. A 0.3-m long quartz (1/2"stainless steel tube used for high pressure) reactor tube (6.35-mm o.d., 4.0-mm i.d.), with a quartz thermocouple well, was used with 0.01-0.5 grams of catalyst (-28/+48 mesh) held in place by quartz wool. A thermal conductivity detector was used with a 3.66-m by 3.2-mm-o.d. stainless steel HayeSep C (80/100 mesh) column at isothermal oven temperatures of 54EC. Argon was used as carrier gas in the GC column at 20 ml/min.

Temperature-programmed oxidation (TPO) of deposited carbon after the reaction was performed by heating the sample from 25 to 900^{J}C at a rate of 20^{J}C /min in flow of 2% oxygen in helium (40 cc/min). The exit gases were monitored by a quadrupole mass spectrometer.

3.   RESULTS AND DISCUSSION

Thermodynamic calculations for the endothermic reaction of CO_2 with CH_4 (fH_{298} = 59.1 kcal/mol), containing a mixture of CH_4, CO_2, H_2O, CO and H_2, indicated that the equilibrium amount of carbon decreases with increasing temperature and increases with increasing pressure, Figure 1.
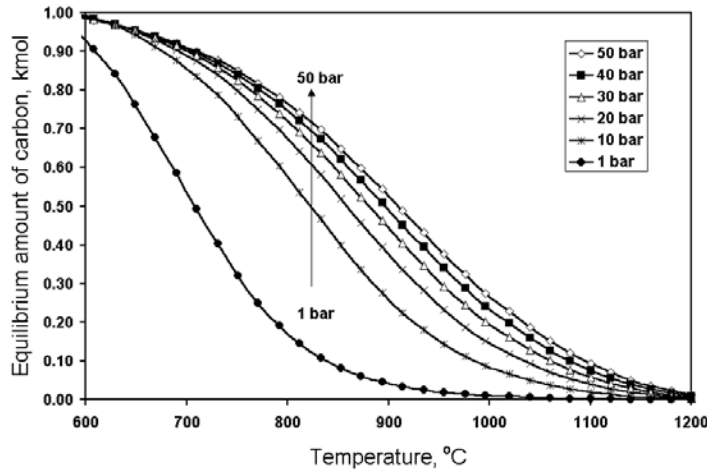
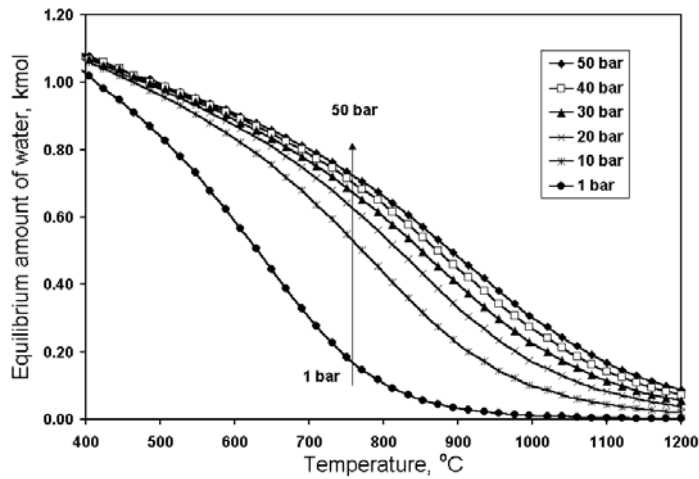Figure 1. Effects of temperature and pressure on equilibrium amount of carbon for CO_2 reforming of methane.

Figure 2. Effects of temperature and pressure on equilibrium amount of water for CO_2 reforming of methane.

A similar result was obtained for water formation at higher pressures as shown in Figure 2. At atmospheric pressure water disappears at temperatures above 900$^{\prime}$C. The high concentration of water is mainly due to the reverse water gas shift (RWGS) reaction and results in a lower H_2/CO ratio. Both water and carbon are by-products of dry reforming and the goal is to develop a catalyst that prevents the net formation of these products. In methane dry reforming, CH_4 decomposition (fH$_{298}$ = 17.89 kcal/mol) and CO disproportionation (fH$_{298}$ = -41.21 kcal/mol) are the two major reactions that contribute to carbon formation. To see which carbon forming reaction contributed most as a function of temperature and pressure, thermodynamic calculations were performed on the individual reactions [15]. Calculations on the CH_4 decomposition reaction showed that as the temperature increased the equilibrium amount of carbon increased. However, increasing the pressure decreased the amount of carbon deposited by this reaction. The same calculation performed on the CO disproportionation reaction indicated that the equilibrium amount of carbon decreased with increasing temperature, but increased with increasing pressure. These results suggest that the later reaction (CO disproportionation) becomes a larger contributor to carbon deposition on dry reforming catalysts used at high pressure. These calculations were done using Gibbs energy minimization method [16], assuming carbon as a pure substance and water in the gas phase. This result
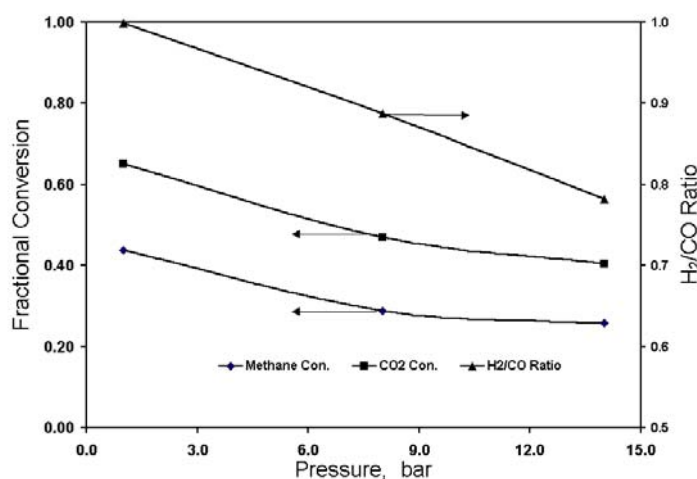

Figure 3. Effect of pressure on methane and CO_2 conversions and H_2/CO ratio over 1wt% Rh/alumina, CO_2/CH_4 = 0.5.

is also in good agreement with a previously published study [17] involving thermodynamic calculations of the effect of pressure on carbon formation during CO_2 and steam reforming of methane.

The reforming of methane with CO_2 was studied over Rh/alumina (1wt%Rh), Pt/ZrO_2 (1.5wt% Pt), and Ce-promoted Pt/ZrO_2 (1wt%Pt, 5wt%Ce) catalysts at 1, 8, and 14 bar. These catalysts have been studied extensively by other researchers at atmospheric pressure [18,19]. However, there are not sufficient data available to evaluate the performance of these catalysts at higher pressures, a requirement for developing an efficient and cost effective commercial process. These catalysts, that operate relatively carbon free at atmospheric pressures, have been tested for production of synthesis gas via methane dry reforming at high pressures.

The effect of pressure on methane and CO_2 conversions as well as on H_2/CO ratio over Rh/alumina catalyst is depicted in Figure 3. It was found that high pressures resulted in lower methane and CO_2 conversions and a lower H_2/CO ratio. The CO_2 conversion was always higher than the methane conversion, this is primarily due to RWGS reaction, but also to carbon gasification by CO_2. H_2/CO ratios of less than 0.8 were measured at a pressure of 14 bar. The stability of the catalyst as a function of time was also tested at 1, 8, and 14 bar and the results for methane conversion are shown in Figure 4. The rate of catalyst deactivation was observed to increase with increasing pressure. The specific rates of deactivation increased from 0.3 to 0.6 and 0.9% per hour for pressures of 1, 8 and 14 bar, respectively.
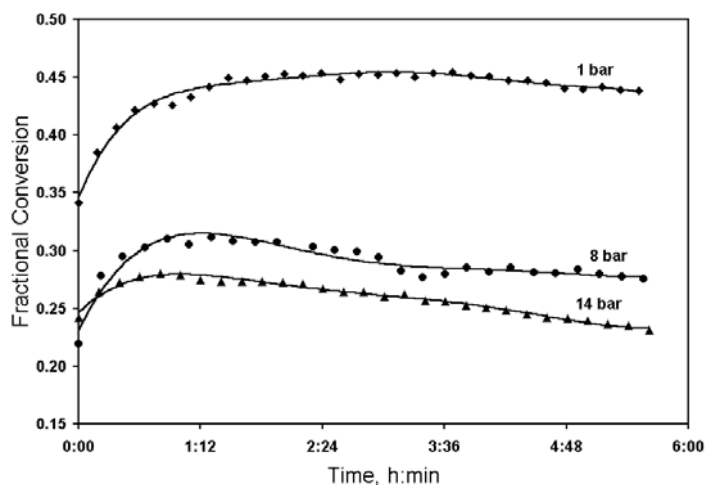

Figure 4. Effect of pressure on methane conversion over 1wt% Rh/alumina, $CO_2/CH_4 = 0.5$.

Similar results to those obtained with the Rh/Al_2O_3 catalyst were found in the case of the Pt/ZrO_2 catalyst. The effect of pressure on methane and CO_2 conversions as well as on H_2/CO ratio over Pt/ZrO_2 catalyst is shown in Figure 5. High pressure resulted in lower methane and CO_2 conversions and
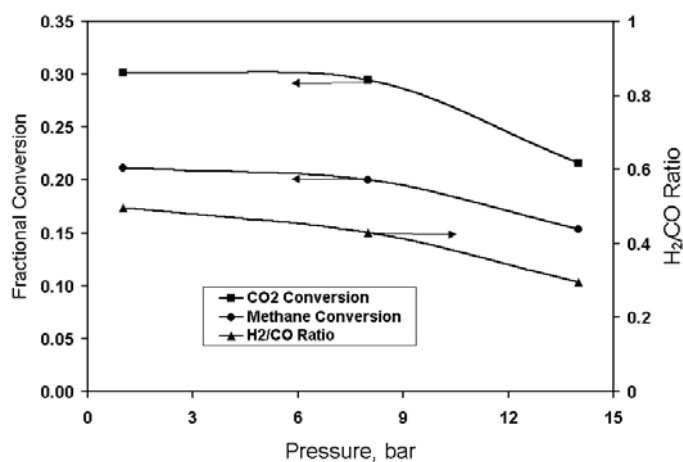

Figure 5. Effect of pressure on methane and CO_2 conversions and H_2/CO ratio over Pt/ZrO_2, $CO_2/CH_4 = 1.14$.
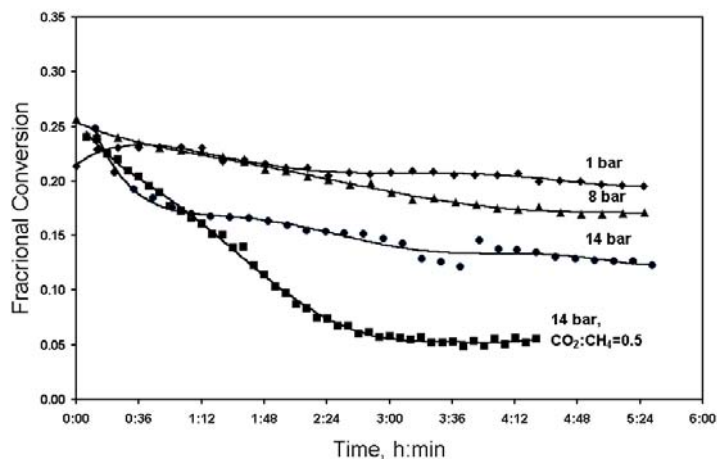

Figure 6. Effect of pressure on methane conversion over Pt/ZrO_2, $CO_2/CH_4 = 1.14$.

a lower H_2/CO ratio. Again, the CO_2 conversion is higher than the methane conversion, as with the Rh/alumina catalyst, due to the RWGS reaction and carbon gasification by CO_2. An H_2/CO ratio of less than 0.3 was measured at a pressure of 14 bar.
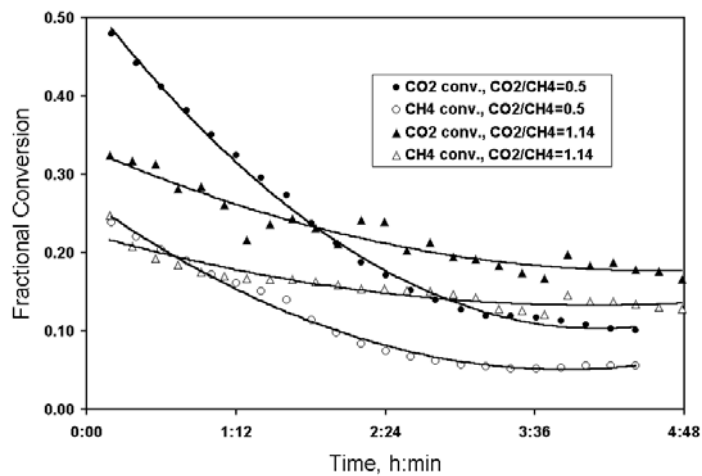

Figure 7. Effect of CO_2/CH_4 feed ratio on methane and CO_2 conversions over Pt/ZrO_2 at 14 bar.
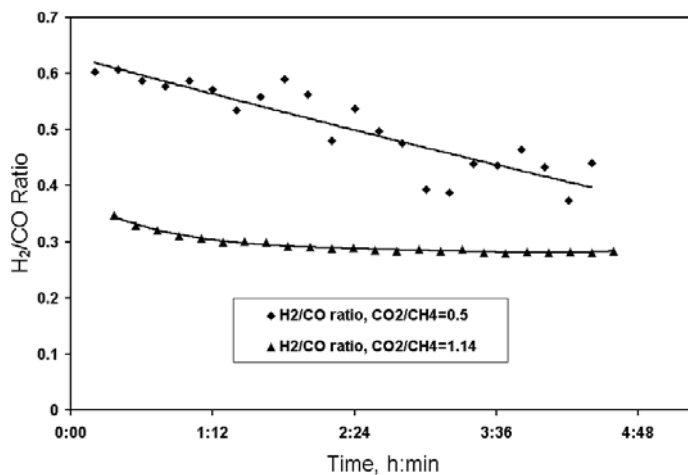

Figure 8. Effect of CO_2/CH_4 feed ratio on H_2/CO ratio over Pt/ZrO_2 at 14 bar.

The stability of the catalyst as a function of time at 1, 8, and 14 bar was also studied and the results for methane conversion are shown in Figure 6. Again, higher catalyst deactivation was observed as the pressure increased from 1 to 8 and 14 bar. The deactivation rates were 0.6, 1.6 and 2.6% per hour at 1, 8 and 14 bar respectively. The deactivation rate was further increased to 4.2%/h when the CO_2/CH_4 feed ratio decreased from 1.14 to 0.5, suggesting that carbon deposition is one of the major contributors to the catalyst deactivation.

The dependence of CH_4 and CO_2 conversions on CO_2/CH_4 feed ratio for Pt/ZrO$_2$ catalyst is shown in Figures 7. Higher deactivation rates were observed for the feed ratio of CO_2/CH_4 = 0.5, mainly due to higher rates of carbon deposition. The CO_2 conversion was always greater than methane conversion and the difference decreased as more carbon formed and deactivated the catalysts. Higher H_2/CO ratio of 0.5 was observed for the feed ratio of CO_2/CH_4= 0.5 compared to 0.3 for the feed ratio of CO_2/CH_4= 1.14, as shown in Figure 8. Higher hydrocarbon in the feed resulted in higher carbon formation and also decreased the H_2/CO ratio with time on stream.
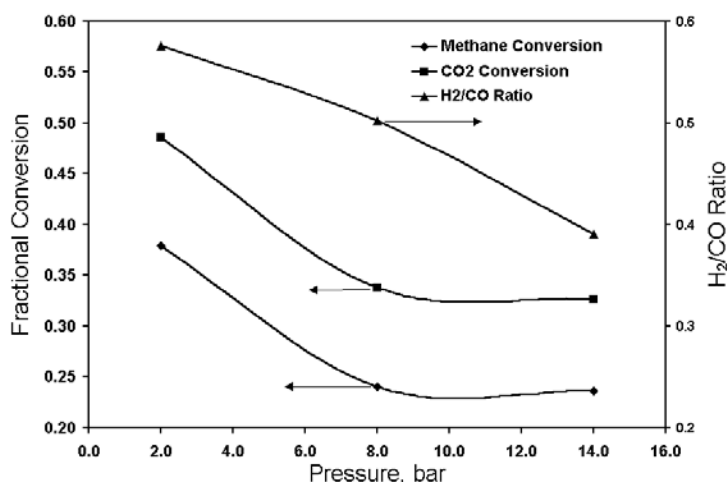

Figure 9. Effect of pressure on methane and CO_2 conversions and H_2/CO ratio over Pt/Ce-ZrO$_2$, CO_2/CH_4 = 1.14.

The effect of pressure on methane and CO_2 conversions as well as on H_2/CO ratio over the Ce-promoted Pt/ZrO$_2$ catalyst is shown in Figure 9. High pressures resulted in lower methane and CO_2 conversions and a lower

H_2/CO ratio. The CO_2 conversion was always higher than the methane conversion. An H_2/CO ratio of less than 0.4 was measured at a pressure of 14 bar. The stability of the catalyst as a function of time at 1, 8, and 14 bar was also studied and the results for methane conversion are shown in Figure 10. Higher catalyst deactivation is observed at elevated pressures with the
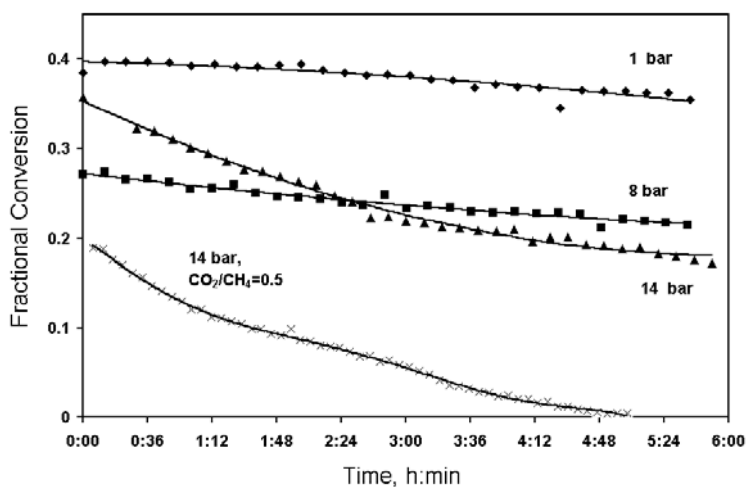

Figure 10. Effect of pressure on methane conversion over Pt/Ce-ZrO$_2$, CO$_2$/CH$_4$ = 1.14.
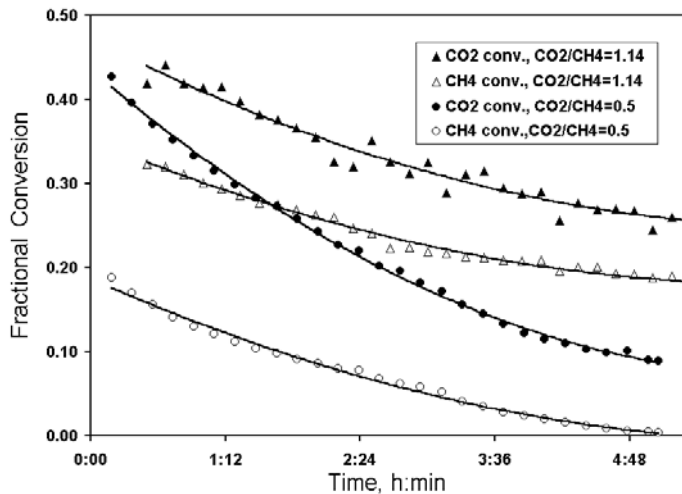

Figure 11. Effect of CO$_2$/CH$_4$ feed ratio on methane and CO$_2$ conversions over Pt/Ce-ZrO$_2$ at 14 bar.

specific deactivation rates being 0.8, 1.1, and 2.6% per hour at 1, 8 and 14 bar, respectively. The deactivation rate was further increased to 3.7%/h when the CO_2/CH_4 feed ratio decreased from 1.14 to 0.5. The dependence of
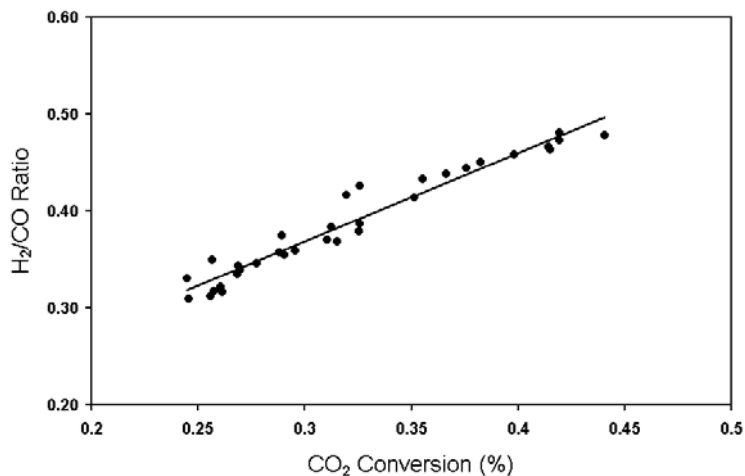

Figure 12. The H_2/CO ratio as a function of CO_2 conversion over Pt/Ce-ZrO$_2$ at 14 bar, $CO_2/CH_4 = 1.14$.
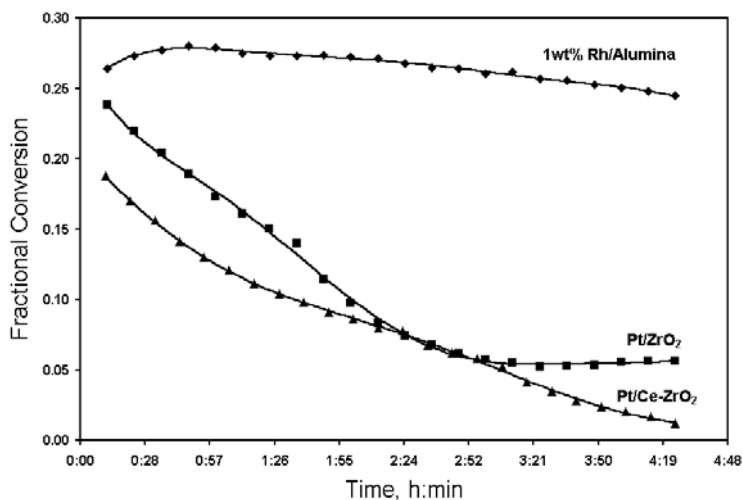

Figure 13. Methane conversion as a function of time on stream at 14 bar, $CO_2/CH_4 = 0.5$.

CH_4 and CO_2 conversions on CO_2/CH_4 feed ratio for Ce-promoted Pt/ZrO_2 catalyst is shown in Figure 11. A higher deactivation rate was observed for the feed ratio of $CO_2/CH_4 = 0.5$ compared to 1.14. The CO_2 conversion was always greater than methane conversion and the differences were lower for the less active catalyst. Higher methane and CO_2 conversions were observed for the feed ratio of 1.14 after 3 hours on stream. The H_2/CO ratios for the Ce-promoted catalyst at 14 bar are plotted as a function of CO_2 conversion and increases with increasing CO_2 conversion as shown in Figure 12. The relationship between these parameters and the H_2/CO ratio of less than one can be attributed to greater influence of the reverse water gas shift reaction.

The stability of the three catalysts with a feed ratio of $CO_2/CH_4 = 0.5$, as a function of time, is compared in Figure 13. The order of reactivity is: Rh/alumina >> $Pt/Ce-ZrO_2$ > Pt/ZrO_2. Both Pt supported catalysts exhibited very high deactivation rates compared to Rh/alumina catalyst, partially due to the rapid deposition of carbon on the surfaces of these catalysts, but also due to metal particle growth [13]. The deactivation rates are 0.9, 3.7, and 4.2%/h for Rh/alumina, Ce-promoted Pt/ZrO_2, and Pt/ ZrO_2 catalysts, respectively. At atmospheric pressure Rh/alumina catalyst produced a H_2/CO ratio of about one, which is greater than those produced by $Pt/Ce-ZrO_2$ (0.57) and Pt/ZrO_2 (0.3). Higher pressure resulted in greater carbon formation, as well as, lower methane and CO_2 conversions and lower H_2/CO ratios. The influence of CO_2/CH_4 feed ratio on H_2/CO ratio was greater for Pt/ZrO_2 than for $Pt/Ce-ZrO_2$. No significant differences are observed for the Ce-promoted catalyst when the CO_2/CH_4 ratio was increased from 0.5 to 1.14, an average H_2/CO ratio of 0.3 was measured in both cases.
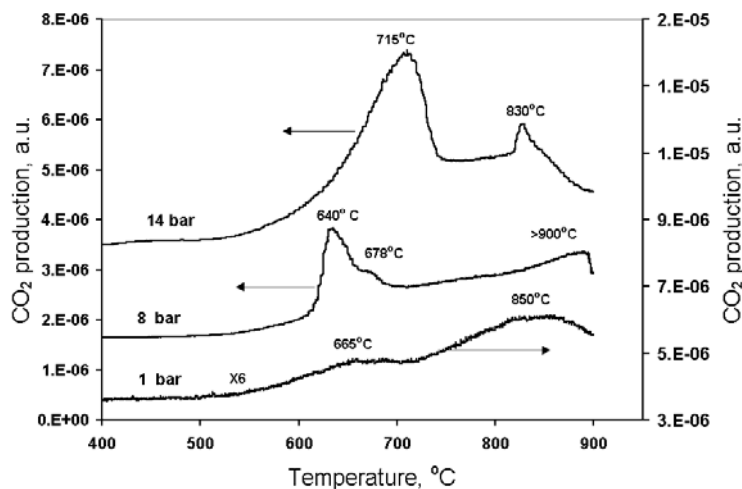

Figure 14. TPO of carbon deposited on $Pt/Ce-ZrO_2$ reacted at $800^{\circ}C$, $CO_2/CH_4 = 1.14$.

Temperature-programmed oxidation (TPO) of the carbon formed on the catalysts was also performed, Figure 14. The results of the TPO experiment on Ce-promoted catalyst reacted at 800°C and 1, 8, and 14 bar, shows different peaks for CO_2 production. The different peaks present in the TPO have been recently characterised by X-ray photoelectron spectroscopy (XPS) and concluded that carbon deposited at two different locations on the catalyst surface [20]. The first peak in each TPO therefore may be either a less stable form of carbon or carbon that formed on a catalyst site that assists in the oxidation of carbon. The second peak may be a more stable form of carbon or one that is formed on a catalyst site that does not assist (i.e. support) in oxidation of the carbon. The low-temperature peak is shifted to higher temperature for the catalyst tested at 14 bar, indicating that as the pressure is increased this carbon becomes less active toward reaction with oxygen or the carbon deposited at the sites that are less active assisting in carbon oxidation. The integration of CO_2 peaks formed during TPO experiments showed that the amounts of carbon on the catalyst also increased with increasing pressure.

4.   CONCLUSIONS

Noble metal catalysts have been tested for production of synthesis gas via methane dry reforming at higher pressures. It was found that high-pressures results in greater carbon formation, lower methane and CO_2 conversions, as well as a lower H_2/CO ratio. Temperature-programmed oxidation (TPO) of the carbon formed on the catalysts indicated that the amounts of carbon on the catalyst increased with increasing pressure. The experimental results presented in this paper are in good agreement with published results of thermodynamic calculations [17] dealing with the effect of pressure, CO_2/CH_4 ratio on methane and CO_2 conversions, H_2/CO ratio, and on carbon formation, as well as with our own thermodynamic calculation results.

ACKNOWLEDGEMENT

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